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NON CONCERTED PATHWAYS IN THE GENERATION OF DEHYDROARENES BY THERMAL DECOMPOSITION OF DIARYLIODONIUM CARBOXYLATES[1].

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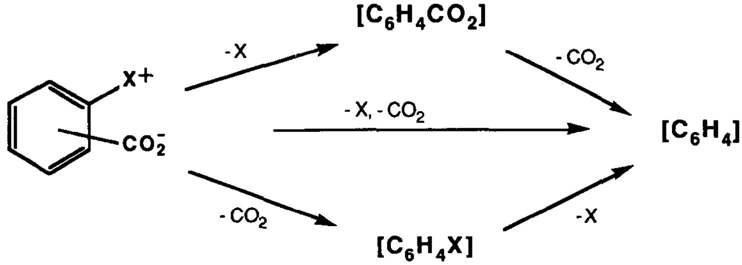
Abstract - 1,3-Dehydrobenzene, 1,4-dehydrobenzene and 2,3-dehydronaphthalene are generated in the thermal decomposition of appropriate diaryliodonium carboxylates as demonstrated by the use of the three phase test. Intermediate species $C_6H_4CO_2$ for *m*- and *p*-benzyne and $C_{10}H_6CO_2$ for 2,3-naphthalyne have been unambiguously trapped in the same way, showing how non-concerted processes are the main pathway for generation of arynic intermediates from those iodonium salts.

Thermal decomposition of benzoic acids *ortho*-substituted with nucleofugic leaving groups has been one of the most general and useful methods for the generation of arynic intermediates[2,3,4] (Scheme I). In this heterolytic fragmentation X^+ has to be a good leaving group such as diazonium[5], aryliodonium[3,6], halogen[7], triazene[4,9], etc.. A central question in such processes is the study of the detailed mechanism of fragmentation and the nature of the intermediates. The exact mechanism is usually unknown and, as shown in scheme I for the generation of dehydrobenzenes, different pathways, concerted and non-concerted (via the intermediates $C_6H_4CO_2$ or C_6H_4X), can be considered.

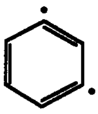
Scheme I

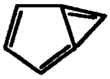


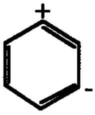
The three phase test[9] has been a useful tool for the study of reactive intermediates, and the existence of several dehydrobenzenes as free species in solution has been demonstrated by this method[3,4]. In the present work, this test has been applied to demonstrate the generation of 1,3- and 1,4-dehydrobenzene as well as 2,3-dehydronaphthalene, and to show how non-concerted pathways are important in the fragmentation process.

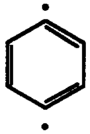
Methods and Results:

1,3- and 1,4-dehydrobenzene. Compared to 1,2-dehydrobenzenes, 1,3- and 1,4-dehydroarenes have been subject to much less study. Different structures can be postulated for these species as shown for the parent compounds *m*-benzyne (**1**) and *p*-benzyne (**2**)[10,11-14].

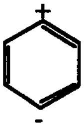

1a


1b


1c

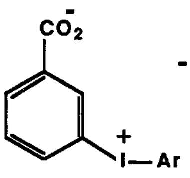

2a


2b


2c

Thus, Bergman[11] reported the generation of a biradical 1,4-dehydrobenzene (**2a**) in the rearrangement of *cis*-1,5-hexadiyn-3-ene and Breslow[12] described the formation of butalene (**2b**) (bicyclo[2.2.0]hexatriene) from Dewar chlorobenzenes. In a similar approach, Wasburn[13] studied the possibility of generation of bicyclo[3.1.0]hexatriene (**1b**) in the bis-dehydrohalogenation of 4,6-dihalobicyclo[3.1.0]hexene. On the other hand, the reported generation of those intermediates in 1,3- and 1,4-elimination or fragmentation reactions from benzene derivatives is almost limited to studies on the thermal or photoinitiated decomposition of diazonium benzene-3- and 4-carboxylates[14], where, in a few cases, zwitterionic structures (**1c**, **2c**) have been also proposed.

In our studies on 1,2-dehydroarenes[3], diaryliodonium carboxylates have shown themselves to be one of the most useful precursors, and so the synthesis of several diaryliodonium 3- and 4-carboxylates was attempted. These precursors were obtained by condensation of an iodoso compound and an arene in acidic media in a similar way as described for related *o*-derivatives[6,15]. Results are summarized in **Table I**



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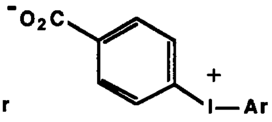


4

a) Ar = C_6H_5
b) Ar = $p\text{-}CH_3\text{-}C_6H_4$
c) Ar =

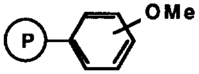


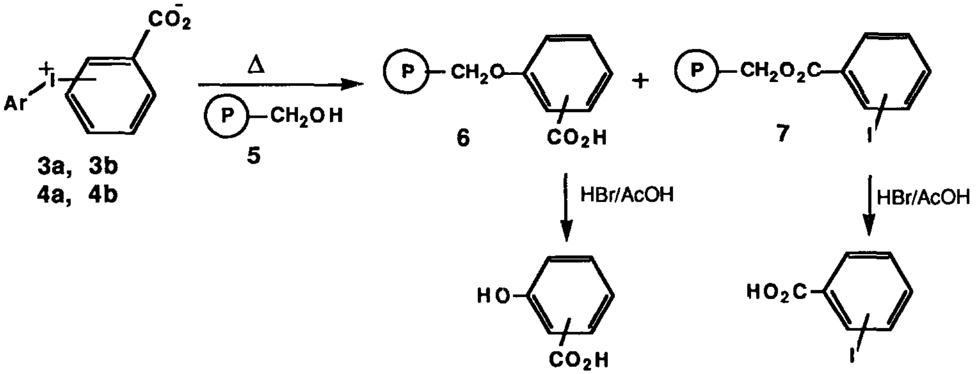
Table I. Yields in the synthesis of diaryliodonium 3- and 4-carboxylates

Compound	Yield (%)
3a	40
3b	77
3c	40
4a	44
4b	22
4c	38

Polymers **3c** and **4c** were prepared by condensation of *m*- or *p*-iodosylbenzoic acid[16] with a polymer containing methoxyphenyl groups[3], in the presence of a mixture of acetic and trifluoroacetic acids with a small amount of sulphuric acid. Neutralization with triethylamine afforded the betainic structures **3c** and **4c**. When the starting resin was one with a functionalization degree of 1.98 mequiv./g (PS-DVB, 2% crosslinked), polymeric precursors were obtained with a functionalization degree of 0.6-0.7 mequiv./g.

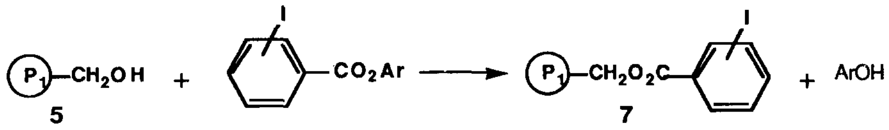
Thermal decomposition of non polymeric precursors **3** and **4** produces a complex mixture of products with a content high in polymeric materials. Trapping of the reactive species generated was attempted with nucleophiles and dienes. In general, reaction with nucleophiles has been described as the principal one for intermediates **1** and **2**[11-14]. However, Breslow[12] has reported the reaction of butalene (**2c**) with diphenylisobenzofurane. In our experiments, no adducts were obtained when precursors **3** and **4** were heated in the presence of several dienes. When the trapping agent was the potassium salt of furoic acid, phenyl furoate was isolated, suggesting the existence of a nucleophilic attack on the iodonium salt or, rather, the preference of the intermediate for nucleophilic trapping agents. Reaction of o-benzynes with carboxylic acids and alcohols[5], as well as with phenols and thiophenols[7b] has been reported to occur in fair yields. A hydroxybenzylic resin (**5**), easily prepared from Merrifield's polymers and whose reaction with o-benzyne has been described[4], was chosen for our studies as a nucleophilic trap. The heating in diglyme (150-160ºC) of a non polymeric precursor **3** or **4** in the presence of resin **5** afforded a polymer whose IR showed the presence of C=O bands. After hydrolysis of this polymer with HBr/AcOH, the respective *m*- or *p*-hydroxybenzoic acids and *m*- or *p*-iodobenzoic acids were isolated (**Scheme II**). Phenol, which would have been the expected product from the trapping of **1** or **2**, was not detected in any case.

Scheme II



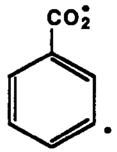
The formation of polymeric esters (**7**) of iodobenzoic acids in small amounts can be explained by reaction between hydroxybenzylic groups and aryl esters of iodobenzoic acids in a transesterification process.

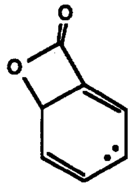
Scheme III

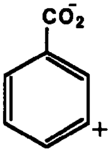


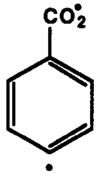
Aryl esters are formed in the thermal rearrangement of diaryliodonium-2-carboxylates, an important side reaction in the thermal fragmentation of those aryne precursors[6], and can also exist in our case, most likely via intermolecular processes. Such a transesterification process was checked to occur when resin **5** was heated in the presence of several esters of benzoic acids under the same conditions as described. Esterification was tested to also occur between hydroxybenzylic resin and iodobenzoic acids in the same experimental conditions.

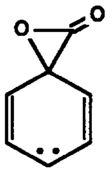
Direct nucleophilic attack by the polymer on the diaryliodonium salt could explain the formation of the polymeric derivatives of *m*- and *p*-hydroxybenzoic acids (**6**). However, the absence of substitution on the other arylic moiety as shown by the non appearance of phenol (from **3a** and **4a**) or *p*-cresol (from **3b** or **4b**) after hydrolysis seems to exclude this process. According to general mechanisms for reactions of nucleophiles with iodonium salts, the alternative pathway is an electron transfer from anion to cation to form a radical pair, and the occurrence of radical intermediates has to be considered[17]. In this way, the formation of polymers **6** would be explained by the intermediacy of a species $C_6H_4CO_2$ with a biradical structure (**8a** and **9a**).

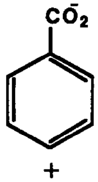

8a


8b


8c


9a

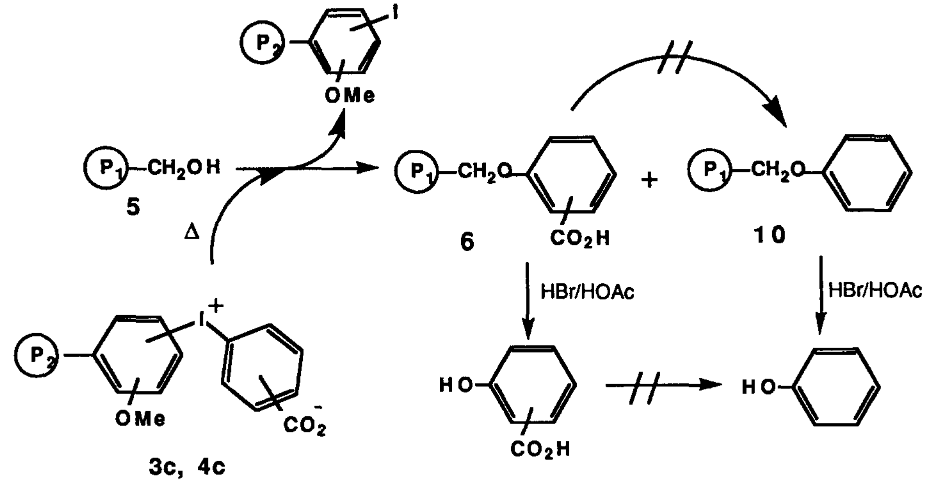

9b


9c

These intermediates should also account for the formation of complex mixtures of polymeric esters as the main product in the thermal decomposition of non-polymeric precursors **3** and **4**. The intermediacy of biradicals **8a** and **9a** as well as the related zwitterionic species (**8c**, **9c**) and the carbenes **8b** and **9b** has been considered in the reported generation of 1,3- and 1,4-dehydrobenzenes via fragmentation processes[14].

The possibility of direct nucleophilic attack on the iodonium salt is excluded in three phase experiments where precursors and trapping agents are bound to different resins. Reaction between functional groups in two different polymers cannot take place except by the intermediacy of a soluble species. Thus, the appearance of an adduct on the trapping resin implies the liberation, from a polymer-bound precursor, of an intermediate which passes through the solution to the second polymer where it is trapped by reaction with its functional groups. When, in a three phase experiment, polymeric precursors **3c** or **4c** were heated in the presence of the hydroxybenzylic resin **5**, IR analysis of the resulting trapping resin again showed the presence of C=O bands. Hydrolysis of this polymer yielded a mixture of phenol and 3- or 4-hydroxybenzoic acids where the latter were always in excess by a ratio of about 5:1.

Scheme IV



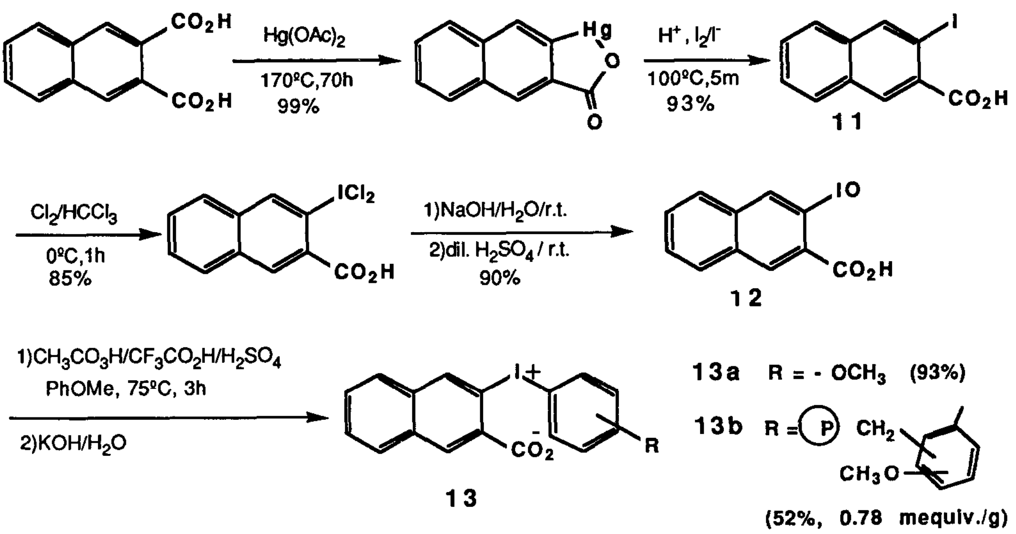
The formation of polymer-bound benzyl carboxyphenyl ether groups (**6**) confirms the intermediacy of species $C_6H_4CO_2$ in the thermal decomposition of diaryliodonium 3- and 4-carboxylates. Decarboxylation of polymeric benzyl carboxyphenyl ether groups to give polymer-bound benzyl phenyl ether groups (**10**) has to be excluded. Heating of the resin containing functional groups **6**, in the same conditions as used for three phase experiments and for longer periods of time, did not produce any decarboxylation. In the same way, conversion of hydroxybenzoic acids to phenol did not occur in the hydrolysis process, as was checked using different samples of benzoic acids. According to these results, the appearance of benzyl phenyl ether functional groups on the trapping polymer requires the occurrence of species C_6H_4: 1,3-dehydrobenzene and 1,4-dehydrobenzene, as free intermediates in solution. Previous works in this field as well as our own experimental data seem likely to agree better with a biradical structure for **1** and **2** but alternative structures cannot be rejected.

Thermal decomposition of diaryliodonium 3- and 4-carboxylates yield 1,3- and 1,4-dehydrobenzenes most likely through decarboxylation of intermediates $C_6H_4CO_2$. Concerted fragmentation of betaines **3** or **4** to give **1** or **2** seems to be excluded as a main pathway because of the absence of any detectable amount of trapped **1** or **2** in two-phase experiments. Those results also suggest that the generation of dehydrobenzenes from species $C_6H_4CO_2$ is a relatively slow process compared to the trapping of the same intermediates by the hydroxybenzylic resin **5** or other reagents. In three phase experiments, higher dilution conditions are reached relative to the ones in two phase experiments. That will favour unimolecular decomposition of the initial intermediates over intermolecular processes. At the same time, reaction of species $C_6H_4CO_2$ with the trapping resin is delayed at least some tenths of a second[18], the time needed to pass from one polymer to the second one. According to this, only in three phase experiments are intermediates **1** and **2** formed and reach the reactive sites of the trapping resin in a great enough amount to be detected.

2,3-dehydronaphthalene. The importance of non-concerted pathways in the generation of *o*-arynic intermediates via heterolytic fragmentations could be demonstrated in the case of 2,3-dehydronaphthalene. The generation of naphthalyne intermediates has been reported in different reactions including several fragmentation processes[19]. For our studies, 2-naphthyl aryliodonium-3-carboxylates were chosen as suitable precursors of 2,3-dehydronaphthalene.

The synthesis of those iodonium salts was accomplished as shown in **Scheme V**. 3-Iodo-2-naphthoic acid (**11**) was obtained in 92% overall yield by reaction of 2,3-naphthalenedicarboxylic acid with mercury(II) acetate and then treatment of the mercurial with I_2/I^- [20]. Oxidation of **11** with chlorine and then hydrolysis with aqueous NaOH followed by careful neutralization with diluted sulphuric acid afforded the iodosoacid **12**. Iodonium salt formation did not take place in the same conditions as those used for the preparation of other iodonium precursors. Finally, reaction of **12** with anisole in the presence of a mixture of peracetic and trifluoroacetic acids, with a small amount of H_2SO_4 gave the expected (4'-methoxyphenyl)-2-naphthyliodonium 3-carboxylate **13a** in excellent yields (93%).

Scheme V



Thermal decomposition of iodonium salts **13** requires temperatures of about 200ºC or higher, as is also the case for similar compounds[3,6]. When the precursor **13a** was heated in the presence of a diene such as tetraphenylcyclopentadienone, the related adduct 1,2,3,4-tetraphenylanthracene[27] (**15**) was obtained in good yields as shown in **table II**, suggesting the occurrence of a 2,3-dehydronaphthalene species (**14**).

Scheme VI

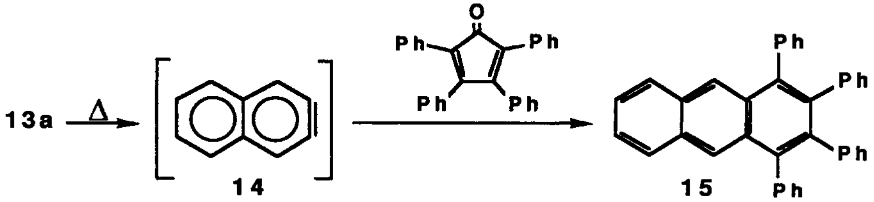


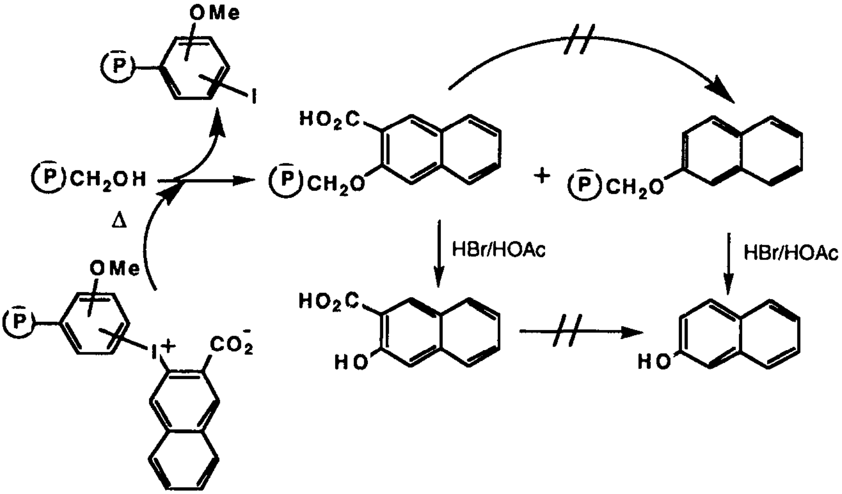
Table II. Thermal decomposition of 13a in the presence of tetraphenylcyclopentadienone[a].

Solvent	temperature(°C)	time	adduct(%)[c]
BrPh	160	4h	**15** (38)[b]
NO_2Ph	211	4h	**15** (41)[b]
None	240 -250	20m	**15** (55)

a) an excess of diene (2-3 times) was used. Some decomposition of diene was observed, specially at higher temperatures. b) based on the betaine actually decomposed. c) yields after isolation and purification

This occurrence was unambigously demonstrated with the use of the three phase test. For this test, a polymeric precursor **13b** was synthesized by reaction between **12** and the resin activated with methoxyphenyl groups[3] (polystyrene 2% crosslinked, 1.98 mequiv./g) in dioxane containing trifluoroacetic acid, peracetic acid and H_2SO_4. In this way, a resin with a functionalization degree of 0.78 mequiv./g of iodonium salt (52% yield for the transformation of methoxyphenyl groups) was obtained.

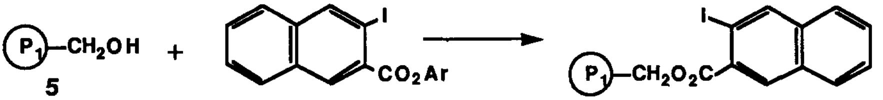
Scheme VII



When the trapping polymer was the hydroxybenzylic resin **5**, in a three phase experiment, results were comparable to the ones obtained for 1,3- and 1,4-dehydrobenzene. Infrared analysis of the polymeric adduct showed the presence of a carbonyl band at ca. 1700 cm^{-1}. Furthermore, treatment with HBr/HOAc afforded not only the product expected for the trapping of 2,3-dehydronaphthalene (2-hydroxynaphthalene) but also 3-hydroxy-2-naphthoic acid. Both products were obtained as an almost equimolecular mixture. These results require the occurrence of an intermediate $C_{10}H_6CO_2$ (**18**) which probably evolves through the loss of CO_2 to form a 2,3-dehydronaphthalene species $C_{10}H_6$ (**14**). Reaction of intermediates such as **18** with thiophenes has been recently considered to explain the low ability of thiophenes (compared to benzene) to trap *o*-benzynes in cycloaddition processes[21]. The formation of **14** could also take place in a concerted process coexisting with the former one. Again, decarboxylation of **16** to **17** or from 3-hydroxy-2-naphthoic acid to 2-hydroxynaphthalene was checked not to occur in our experimental conditions, so that both functional groups in the polymeric adduct have to be formed by reaction of hydroxybenzylic resin **5** with two different intermediates **14** and **18**.

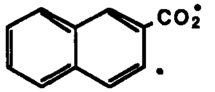
As can be noted, thermal decomposition of polymeric aryl-2-naphthyliodonium-3-carboxylate (**13b**) gives a higher ratio of aryl benzyl ether groups to benzyl carboxyaryl ether groups in the polymeric adduct as compared with polymer-bound arylphenyliodonium 3- and 4-carboxylates (**3c** and **4c**). This fact suggest a faster decomposition of the intermediate $C_{10}H_6CO_2$ (**18**) to the dehydronaphthalene species (**14**) or the lower intermolecular reactivity of the same intermediate **18**. Alternatively, a higher participation of concerted pathways in the generation of 2,3-dehydronaphthalene can be considered. Two phase experiments confirm the former data. When (4'-methoxyphenyl)-2-naphthyliodonium-3-carboxylate (**13a**) was decomposed in the presence of hydroxybenzylic resin **5**, infrared analysis of the polymeric adduct showed the presence of a complex carbonyl band. After hydrolysis with HBr/HOAc, 3-hydroxy-2-naphthoic acid was obtained, but 2-hydroxynaphthalene was also formed, being the former in excess by a ratio of about 9:1 . 3-Iodo-2-naphthoic acid was detected as a very minor product. Again, transesterification of hydroxybenzylic groups with the 3-iodo-2-naphthoic ester formed in the rearrangement of the initial iodonium salt **13a**[6] would explain the appearance of this compound.

Scheme VIII

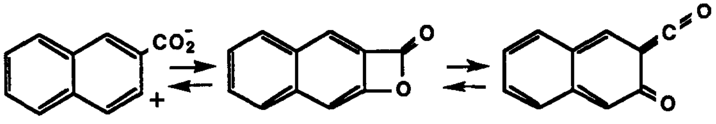


5 **17**

The exact nature of the intermediate $C_{10}H_6CO_2$ is difficult to assess, but according to previous works[2] different structures can be considered: a diradical one (**18a**) or the ones corresponding to the zwitterion **18b** and its valence tautomers, the ketene **18d** and the naphtho[2,3-b]oxet-2-one **18c**.



18a



18b **18c** **18d**

Diradical intermediates such as **18a** have been considered as precursors of *o*-benzyne[22] and would explain most of the experimental results. Recent studies on naphtho[2,3-b]oxet-2-one[23] showed how alcohols react with **18c** to give esters of 3-hydroxy-2-naphthoic acid. In our case, ester groups are absent in the polymeric adduct formed in three phase experiments, as shown by IR and by the fact that hydrolysis to give 2-naphthol and 3-hydroxy-2-naphthoic acid is only possible by the use of reagents and conditions characteristic for the cleavage of ether linkages. On the other hand, zwitterionic structures such as **18b** have been described, rather surprisingly, to react with benzyl alcohol in a very different way[24] and a different reaction is also to be expected for **18d**.

Kinetic studies. Thermal decomposition of the previously described polymeric iodonium salts can be easily monitored by infrared spectroscopy through disappearance of carboxylate bands. A direct relationship exits between the loading of functional groups in the resin and the intensity of those bands when using, as an internal standard, a band characteristic of the polymeric backbone. A_r can be defined as the intensity ratio (in absorbance units) between both bands, and, for an unimolecular decomposition of functional groups, an exponential decrease in the value of A_r is to be expected[4] according to the expression $A_r = A_r^o e^{-kt}$. A_r^o is the initial value for A_r and k represents the rate constant for such a decomposition. Data obtained in this way for polymeric diaryliodonium 3- and 4-carboxylates at 120 ºC are shown in **Figure 1** as well as the ones for polymeric aryl-2-naphthyliodonium-3-carboxylate at 165 ºC. For **3c** and **4c** the band selected as characteristic for the iodonium salt was the one at 1368 cm^{-1}, using the polymer bands at 1407-1524 cm^{-1} as reference. For **13b** the carboxylate band of iodonium groups at ca. 1600 cm^{-1} was used with the same reference bands.

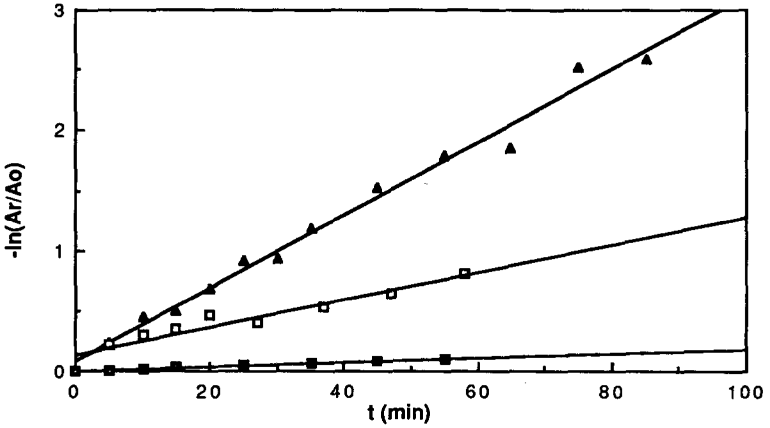


Figure 1. Kinetic data for decomposition of polymeric diaryliodonium-3-carboxylate (▲) and 4-carboxylate (□) at 120ºC, and for polymeric 2-naphthyliodonium-3-carboxylate at 165ºC (■).

Table III. Arrhenius parameters for decomposition of polymeric precursors of arynic intermediates.

Intermediate	Ea(Kcalmol^{-1})	A (s^{-1})
m-benzyne	25.4	$7.6\ 10^{10}$
p-benzyne	20.7	$6.6\ 10^{7}$
2,3-naphthalyne	28	$2.7\ 10^{9}$
o-benzyne	32.9	$1.9\ 10^{12}$

Kinetic analysis at several temperatures for each precursor allowed kinetic and activation parameters to be determined. **Table III** presents Arrhenius parameters, including the ones for a related *o*-benzyne precursor calculated by thermogravimetry[25]. **Table IV** shows activation parameters determined for experiments included in Figure 1 .

Tabla IV. Kinetic parameters for decomposition of polymeric precursors of arynic intermediates.

Intermediate	T	k(s^{-1})	$\Delta G^{\ddagger}$(Kcal mol^{-1})	$\Delta H^{\ddagger}$(Kcal mol^{-1})	$\Delta S^{\ddagger}$(cal mol^{-1}°K^{-1})
m-benzyne	393	$5.16\ 10^{-4}$	29.1	24.6	-11
p-benzyne	393	$1.89\ 10^{-4}$	29.9	19.9	-25.4
2,3-naphthalyne	438	$3.13\ 10^{-5}$	35	27.1	-18
o-benzyne	478	$22.6\ 10^{-4}$	34.5	31.9	-6

As mentioned above, fragmentation of diphenyliodonium carboxylates has been reported to be accompanied by a rearrangement to give esters of iodobenzoic acids[3,6,25]. The occurrence of this side reaction for polymeric precursors can be tested by the presence of a new C=O ester band in the IR of decomposed salts. The absence of this band confirms that no rearrangement occurs in the fragmentation process of resins **3c**, **4c** and **13b**. Intramolecular rearrangement is not possible in diaryliodonium 3- and 4-carboxylates and intermolecular processes are hindered by dilution and immobilization effects caused by the polymeric backbone. The first limitation does not apply to naphthyliodonium salt **13b**, but the nature of the aromatic group involved is essential in determining the participation of such a rearrangement, as was observed for substituted aryliodonium-2-carboxylates[3]. According to the method, rate constants calculated will include all unimolecular processes for which carboxylate group is loss: $k_{obs} = \Sigma\, k_i$.

Kinetic data are compatible with the suggested mechanisms. Decomposition, at appreciable rates, of diaryliodonium 3- and 4-carboxylates takes place at lower temperatures than for *o*-carboxylates, which most likely reflects the lower stability of those iodonium salts. Data for naphthyliodonium salt are comparable with the ones for *o*-benzyne precursors[3,4]. In general, fragmentations of these compounds are best carried out at temperatures higher than 150 ºC.

Conclusions

1,3-Dehydrobenzene, 1,4-dehydrobenzene and 2,3-dehydronaphthalene are generated in the thermal decomposition of the appropriate diaryliodonium carboxylates, as demonstrated by the three phase test. The whole set of data agree better with a non-concerted pathway for the generation of those species: an intermediate with a composition $C_6H_4CO_2$ for dehydrobenzenes and $C_{10}H_6CO_2$ for dehydronaphthalene is initially formed and decomposes to yield a dehydroarene and CO_2. The concerted fragmentation process in which an dehydroarene, CO_2 and an iodoarene are simultaneously formed cannot be ruled out, however the non-concerted pathway should be the main one. Generation of 2,3-dehydronaphthalene from the initial intermediate $C_{10}H_6CO_2$ seems to be faster than in the case of *m*- and *p*-benzyne. That could be discussed in terms of the greater stability of *o*-benzynes as compared to *m*- and *p*-dehydrobenzenes[10]. An increasing participation of the concerted pathway in the formation of *o*-dehydroarenes can also be considered to explain the experimental results.

The exact nature of the intermediates $C_6H_4CO_2$, $C_{10}H_6CO_2$, C_6H_4 and $C_{10}H_6$ cannot be definitively established. The participation of diradical structures can be reasonably proposed, but some others can also be considered.

Experimental Section

Diphenyliodonium-3-carboxylate (3a). 3-Iodobenzoic acid (10.0 g, 0.04 mol) was dissolved in 100 ml of concentrated H_2SO_4. The solution was cooled to -10ºC and potassium persulphate (21.6 g, 0.08 mol) was added in small portions. When addition was complete, stirring was continued for 15 min. and then benzene (50 ml) was added and the mixture stirred at -5 ºC for 1 h. After 3 h at 0 ºC, ice water (100 ml) was added and the pH was carefully adjusted to ca. 9 by dropwise addition of ammonium hydroxide, keeping the temperature as close as possible to 0 ºC. The precipitate was filtered, washed with water and dried (5.2 g, 40%). m.p. : 200-201 ºC (water). IR (KBr): 3040, 1575, 1540, 1360, 990, 840, 760, 730 cm^{-1}. MS, m/e: 324, 248, 231(100%), 204, 77.

In the same way the following diaryliodonium 3- and 4-carboxylates were prepared:

Diphenyliodonium-4-carboxylate (4a): From 10 g of 4-iodobenzoic acid, 5.66 g (44%) of **4a** were obtained. m.p.: 210-211 ºC dec. (water) (lit[15b]: 210 ºC). IR (KBr): 3040, 1575, 1530, 1360, 990, 820, 760, 730 cm^{-1}. MS, m/e: 324, 280, 248, 204, 121, 77(100%).

(4'-Methylphenyl)phenyliodonium-3-carboxylate (3b): From 5.0 g of 3-iodobenzoic acid and toluene instead of benzene, 5.19 g (77%) of **3b** were obtained. m.p.: 213-214 ºC dec. (water). IR (KBr): 3030, 1590, 1570, 1530, 1350, 1330, 1110, 980, 830, 780, 730, 700, 690 cm^{-1}. MS, m/e: 248, 218 (100%), 127, 91.

(4'-Methylphenyl)phenyliodonium-4-carboxylate (4b): From 10.0 g of 4-iodobenzoic acid and toluene, 3 g (22%) of **4b** were obtained. m.p.: 230-231 ºC dec. (water). IR (KBr): 3040, 1580, 1540, 1370, 1000, 860, 825, 800, 765, 695 cm^{-1}. MS, m/e: 338, 248, 218 (100%), 127, 91.

Polymeric diaryliodonium-3-carboxylate (3c). 3-Iodosylbenzoic acid (3.72 g, 14 mmol) was dissolved in a mixture of glacial acetic acid (40 ml), trifluoroacetic acid (6 ml) and concentrated H_2SO_4 (1.5 ml). A polystyrene-2% divinylbenzene polymer containing methoxyphenyl groups (2 g, 1.98 mequiv./g, 3.96 mequiv.) was stirred in this solution at 40-50 ºC for 96 h. The reddish resin was filtered and washed with acetic acid and then ethanol and ethanol/CH_2Cl_2 (1/5) until neutral pH of filtrates. After this, the polymer was treated with Et_3N/CH_2Cl_2 (1/10) three times, for 15 minutes each time, at room temperature, and then washed with ethanol, ethanol/CH_2Cl_2 (1/5, until neutral pH), CH_2Cl_2 and acetone and vacuum dried to constant weight. By weight increase and thermogravimetry[25] a functionalization degree of 0.66 mequiv./g was calculated (40% conversion of methoxyphenyl groups). IR (KBr): 3016, 2914, 1590, 1573, 1536, 1358, 815, 751, 698 cm^{-1}.

Polymeric diaryliodonium-4-carboxylate (4c): From 4-iodosylbenzoic acid, this polymer was prepared as described for **3c**, to give 2.37 g of a resin with a functionalization degree of 0.63 mequiv./g (38% conversion of methoxyphenyl groups).

Thermolysis of 3b in the presence of potassium furoate. (4'-methoxyphenyl) phenyliodonium-3-carboxylate (0.1 g, 0.3 mmol) and potassium furoate (0.3 g, 2 mmol) were mixed and heated in an argon atmosphere at 210 ºC for 15 min.. The resulting mixture was extracted with ether and the ethereal extract chromatographed on silica to give, as main products, phenyl furoate and *p*-iodotoluene, identical with authentic samples.

Thermolysis of 4b in the presence of potassium furoate. Starting from (4'-methoxyphenyl)phenyliodonium-4-carboxylate, and as described for **3b**, phenyl furoate and *p*-iodotoluene were again isolated.

Thermolysis of 3b in the presence of hydroxybenzylic resin (5). (4'-methoxyphenyl)phenyliodonium-3-carboxylate (1.4 g, 4.14 mmol) and hydroxybenzylic resin (PS-2%DVB, 2.4 mequiv./g) (0.62 g, 1.47 mequiv.) were added to diglyme (50 ml) and the mixture was heated under reflux for 24 h. The polymer was filtered, washed with ethanol, acetone and ether and dried to constant weight. IR (KBr): 2900, 1740-1680, 1350, 1230, 1180, 810, 740, 690 cm^{-1}.

The former resin (0.67 g) was heated under reflux, for 48 h, in acetic acid (30 ml) saturated with HBr. The polymer was filetered, washed with ethanol, acetone and ether and dried. The resulting resin showed the formation of benzylacetate groups, IR (KBr): 1740, 1600, 1490, 1380, 1365, 1220 cm^{-1}.

The combined filtrates were vacuum distilled and the residue was subjected to preparative thin layer chromatography on silica to give 3-hydroxybenzoic acid (28 mg) and 3-iodobenzoic acid (4 mg). No phenol could be detected.

Thermolysis of 4b in the presence of hydroxybenzylic resin (5). Thermolysis was carried out as described for **3b**, and after washing and drying, the resin showed IR bands (KBr) at 2910, 1730-1680, 1600, 1490, 1420, 1260, 1200, 1160, 1060, 1010 cm^{-1}. After treatment with HBr/HOAc as described, 4-hydroxybenzoic acid and 4-iodobenzoic acid were isolated from solution by preparative TLC. Again, no phenol was detected.

Thermolysis of 3b or 4b in the presence of polymeric furoate. The iodonium salt (**3b** or **4b**) (1.5 g, 4.4 mmol) and polymeric furoate[3] (PS-2%DVB, 2.77 mequiv./g) (1.08 g, 3 mequiv.) were suspended in diglyme (50 ml) and the mixture was heated under reflux for 24 h. The polymer was filtered, washed with ethanol, acetone and ether and vacuum dried. No changes were observed in the IR of this resin relative to polymeric furoate.

The former resin was suspended in a mixture of methanol (50ml) and water (40 ml) containing KOH (4.5 g) and heated under reflux for 48 h. The polymer was filtered, washed with water/methanol, methanol, ethanol, acetone and ether and dried to give a hydroxybenzylic resin. The filtrate was concentrated, acidified and extracted with ether. The ethereal solution was concentrated to give furoic acid as the only product.

Three phase tests. Dehydrobenzene transfer between polymeric iodonium salts (3c or 4c) and hydroxybenzylic resin (5). Polymeric diaryliodonium 3- or 4-carboxylate (**3c** or **4c**) (2.0 g, 1.2-1.3 mequiv.) and hydroxybenzylic resin (0.4 g, 0.96 mequiv.) separated by porous plates were suspended in diglyme and heated under reflux for 24 h. Both polymers were separated and washed with ethanol, acetone and ether. The trapping polymers showed IR bands (KBr) at 1700, 1455, 115, 1020, 820, 755, 700 cm^{-1}. Afterwards, the trapping resin was refluxed for 48 h in acetic acid (15 ml) saturated with HBr. The polymer was filtered, washed with ethanol, acetone and ether and dried to give a resin with benzylacetate groups. The combined filtrates were vacuum distilled and the residue was subjected to TLC on silica.

From polymeric diaryliodonium-3-carboxylate (**3c**), 3-hydroxybenzoic acid (ca. 14 mg) and phenol (ca. 3 mg) were obtained.

From polymeric diaryliodonium-4-carboxylate (**4c**), 4-hydoxybenzoic acid and phenol were obtained in similar amounts.

3-Iodo-2-naphthoic acid (11). 2,3-naphthalenedicarboxylic acid (7 g, 32.4 mmol) was added to a hot solution of NaOH (2.6 g, 65 mmol) in water (26 ml). A solution of mercury(II) acetate (11.34 g, 35.6 mmol) in water (23 ml) and glacial acetic acid (1.5 ml) was prepared by heating the mixture and filtering while hot. Both hot solutions were mixed in a 250 ml flask and introduced in an oil bath whose temperature was raised to 170 ºC. Carbon dioxide evolution was observed and care had to be taken to avoid any loss of material. Heating was continued for 70 h. On cooling, the precipitate was filtered, washed with water and methanol and dried to give anhydro-3-hydroxymercuri-2-naphthoic acid (11.9 g, 99%). IR (KBr): 1550, 1530, 1430, 1365, 1320, 1285, 880, 799, 775, 730 cm^{-1}.

Anhydro-3-hydroxymercuri-2-naphthoic acid (10 g, 27 mmol) was added in small portions to a hot solution of 1N NaOH (50 ml). The resulting solution was heated to boiling and concentrated HCl (2.6 ml, 28.5 mmol) was slowly added. Heating was discontinued, glacial acetic acid (0.9 ml, 15 mmol) was added and, at this point, a white precipitate formed. A solution of potassium iodide (5 g, 30 mmol) and iodine (7.65 g, 30 mmol) in water (7.5 ml) was added as rapidly as possible to the initial solution and the mixture was heated under reflux for 5 min.. The solution was made alkaline by addition of NaOH (0.6 g, 15 mmol) and filtered to separate the precipitated mercury(II) iodide. The filtrate was acidified with concentrated HCl and the precipitate formed was filtered. The solid was washed with an aqueous solution of potassium iodide and then with water to give 3-iodo-2-naphthoic acid (7.5 g, 93%) after drying. m.p.: 213-215 ºC (ethanol) (lit.[26]: 214 ºC). IR (KBr): 3200-3400, 1680, 1445, 1394, 1282, 1196, 1142, 965, 880, 777, 751, 740 cm^{-1}. ^{1}H NMR (DMSO-d^6) ∂: 7.2-8 (m, 4H), 8.15 (s, 1H), 8.4 (s, 1H). MS, m/e: 298, 281, 253, 171, 126, 125, 115(100%).

3-Iodosyl-2-naphthoic acid (12). Dry chlorine gas was bubbled into an ice-cooled solution of 3-iodo-2-naphthoic acid (2 g, 6.7 mmol) in $HCCl_3$ (25 ml) for 1 h. The yellow crystalline precipitate was filtered, washed with hexanes and dried to give 3-iodosyl-2-naphthoic acid dichloride (2.1 g, 85 %). m.p.: 210 ºC dec.. IR (KBr): 1688, 1641, 1608, 1442, 1330, 1245, 1191, 1135, 1107, 880, 770, 740 cm^{-1}.

The former dichloride (2 g, 5.4 mmol) was dissolved in aqueous NaOH and the solution was carefully acidified with diluted H_2SO_4. The precipitate was filtered washed and dried to give 3-iodosyl-2-naphthoic acid (1.54 g, 90 %) which was crystallized from water. m.p.: 231-232 ºC dec.. IR (KBr): 3420, 2880, 2430, 1590, 1555, 1340, 1304, 1111, 964, 789, 746 cm^{-1}. ^{1}H NMR (F_3CCO_2H) ∂: 7.4-8.5 (m, 4H), 8.35 (s, 1H), 8.8 (s, 1H). Anal. Calc. for $C_{11}H_7IO_3$: C, 42.04; H, 2.23. Found: C, 41.80; H, 2.32.

(4'-methoxyphenyl)-2-naphthyliodonium-3-carboxylate (13a). 3-Iodosyl-2-naphthoic acid (1 g, 3.2 mmol) was added to a mixture of peracetic acid (2 ml), trifluoroacetic acid (2 ml) and H_2SO_4 (0.1 ml). This mixture was stirred at 70-80 ºC and a solution of anisole (0.5 ml, 4.6 mmol) in peracetic acid (2 ml) was added dropwise. The stirring and heating was continued for 2.5 h and then the mixture was poured into ice-water (25 g) and made alkaline with solid KOH. The precipitate was filtered, washed with water and dried to give **13a** (1.2 g, 93 %). m.p.: 220 ºC dec. (water). IR (KBr): 3030, 1580, 1480, 1340, 1290, 1246, 1170, 1012, 790 cm^{-1}. Anal. Calcd. for $C_{18}H_{13}IO_3$: C, 53.47; H, 3.22. Found: C, 53.31; H, 3.28.

Preparation of polymeric aryl-2-naphthyliodonium-3-carboxylate (13b). A polystyrene-2 % divinylbenzene polymer containing methoxyphenyl groups (1 g, 1.98 mequiv.) was suspended in a mixture of trifluoroacetic acid (12.5 ml), peracetic acid (5 ml), dioxane (12 ml) and H_2SO_4 (0.25 ml). The mixture was stirred and heated at 70-80 ºC and 3-iodosyl-2-naphthoic acid (1 g, 3.2 mmol) was added in small portions over a period of 48 h. The resin was filtered and worked up as described for polymeric diaryliodonium-3-carboxylate (**3c**) to give **13 b** (1.3 g, 0.78 mequiv/g, 52 % conversion of methoxyphenyl groups). IR (KBr): 1600, 1492, 1454, 1334, 1245, 1114, 810, 791, 754, 698 cm^{-1}.

Thermolysis of 13a in the presence of tetraphenylcyclopentadienone.

a) (4'-methoxyphenyl)-2-naphthyliodonium-3-carboxylate (**13a**) (1 g, 2.47 mmol) and tetraphenylcyclopentadienone (2.85 g, 7.4 mmol) were mixed and heated under argon in an oil bath at 240-250 ºC. Decomposition was complete after 20 minutes and the residue was extracted with CH_2Cl_2 and ether. The combined solutions were evaporated and the residue chromatographed on silica to give 4-iodomethoxybenzene (0.35 g, 60%) and tetraphenylanthracene (0.66 g, 55 %), m.p.: 293-294 ºC; IR (KBr): 3046, 3014, 1586, 1485, 1438, 1070, 1022, 882, 737, 698 cm^{-1}; ^{1}H NMR (CCl_4) ∂: 8.15 (2 H), 7.3 (12 H), 6.85 (12 H). Small amounts of naphthoic acid and 3-iodo-2-naphthoic acid were also detected.

b) 13a (1 g, 2.47 mmol) and tetraphenylcyclopentadienone (1.9 g, 4.94 mmol) were stirred and heated under reflux in bromobenzene (30 ml) for 4 h. Then, the solvent was vacuum distilled and the residue was extracted with CH_2Cl_2 and EtOAc. Betaine **13a** (0.7 g, 70 %) was recovered from the undissolved solid and tetraphenylanthracene (0.11 g, 38 % based on betaine decomposed) was isolated as described.

When nitrobenzene was used as the solvent, 0.25 g (25 %) of **13a** were recovered and 0.37 g (41 % based on betaine decomposed) of tetraphenylanthracene were obtained.

Thermolysis of 13a in the presence of hydroxybenzylic resin (5). **13 a** (1 g, 2.47 mmol) and hydroxybenzylic resin (0.6 g, 1.43 mmol) were added to bromobenzene (30 ml) and the mixture was stirred and heated under reflux for 48 h. After work-up as described, a polymer was obtained which showed IR bands (KBr) at 2921, 1735, 1690, 1598, 1494, 1450, 1281, 1207, 1100-1000, 820, 748, 698 cm^{-1}. This resin was treated with glacial acetic acid (25 ml) saturated with HBr under reflux for 48 h. After work-up as usual, 3-hydroxy-2-naphthoic acid, 2-hydroxynaphthalene and 3-iodo-2-naphthoic acid were obtained.

Three phase test. Dehydronaphthalene transfer between polymeric naphthyliodonium salt (13b) and hydroxybenzylic resin (5). Starting from polymeric aryl-2-naphthyliodonium-3-carboxylate (1 g, 0.78 mequiv.) and hydroxybenzylic resin (0.2 g, 0.48 mequiv.), the three phase test was carried out as described for precursors **3c** and **4c**. The polymeric adduct showed IR bands (KBr) at 2913, 1699, 1592, 1502, 1488, 1237, 1175, 1029, 807, 751, 697 cm^{-1}. After work-up as usual, 3-hydroxy-2-naphthoic acid and 2-hydroxynaphthalene could be isolated in almost equimolecular amounts. 3-Iodo-2-naphthoic acid could not be detected.

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